



# A New Virial-Theorem-Based Semi-*Ab-Initio* Method for Atomistic Simulations

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## Abstract

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A new semi-*ab-initio* method for atomistic simulations based on the virial theorem has been suggested. The method is completely within the realm of the density-functional theory and uses the so-called "reduced" electron spin-density functional (SDF). The crucial component of the method is the ansatz expressing (for both one-component and two-component systems) the electron density at point  $\mathbf{r}$  as a superposition of "atomic" densities due to the neighboring atoms. The total energy of this system is shown to consist of three terms. The first depends only on the simulation volume and is independent of the atomic configuration. The second and third, like the embedded-atom method (EAM), are the interatomic pairwise interaction energy, and an "N-electron" term, which cannot be expressed as an interatomic interaction; it originates from the electron-correlation interaction. The atomic densities are constructed using a set of polynomial-exponential functions resulting in an analytic form for the pair interatomic potential. The coefficients in the atomic density expressions are found using a calibration procedure based on performing a series of *ab-initio* calculations for a few crystal modifications of this system. Success will depend on whether the charge density in a low-symmetry system under simulation will also be close to the true density obtainable from a meaningful *ab-initio* calculation; then, the simulation results would be identical to those of the corresponding *ab-initio* calculation. To what extent the superposition ansatz satisfies this condition is unclear without experimental confirmation.

## Acknowledgments

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# 1. Introduction

The formulation of the density-functional formalism in the pioneering works of Hohenberg and Kohn (1964), and Kohn and Sham (1965) published almost 35 years ago opened a new era in the quantum-mechanical approach to the physics of condensed matter. The advent of high-speed computers and efficient methods of electronic calculations using the density-functional theory made it possible to achieve tremendous progress in our understanding of electronic and structural properties of both crystalline and amorphous solids.

The density-functional approach requires solving a self-consistent Kohn-Sham quasi-one-particle Schrödinger-like equation. While it is a rather straightforward and easy task for high-symmetry crystalline systems, analysis of low-symmetry states, like crystal-lattice defects, free surfaces, grain boundaries (GBs), etc., is, in most cases impossible now, in spite of proliferation of high-speed supercomputers and efficient *ab-initio* methods. The problem becomes completely intractable when dealing with arbitrary (nonuniform) crystal-lattice deformation, defect relaxation, and analysis of polycrystals.

A family of semi-empirical methods\* emerged during the recent decade, which has made the above problems manageable. In fact, tremendous success has been achieved in atomistic modeling of a great many important systems elucidating processes of atomic relaxation accompanying point defects, impurities, ad-atom layers, GBs and free surfaces, dislocations dynamics, etc. As a triumph of atomistic simulation, new and unsuspected features of dislocation dynamics have been recently discovered (Bulatov et al. 1998).

The efforts in rectifying semi-empirical methods in recent years have been directed at including angle-dependent potentials; this is crucial when treating transition metals and

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\* For references to the most widely used method see the following: the embedded-atom method (Baskes 1997); the Finnis-Sinclair N-body potential (Finnis and Sinclair 1984; Calder and Bacon 1993); the tight-binding fourth-moment method (Carlsson 1990, 1991); the angle-dependent tensor potential, the so-called embedded-defect methods (Simonelly, Pasianot, and Savino 1997); and the bond-order family of potentials (Tersoff 1986, 1989; Aoki, Horsfield, and Pettifor 1997; Krasko, Rice, and Yip, to be published).



semiconductors (Tersoff 1986, 1989; Carlsson 1990, 1991; Aoki, Horsfield, and Pettifor 1997; Simonelly, Pasianot, and Savino 1997). In attempts to make semi-empirical methods as close to *ab-initio* methods as possible, the tight-binding approach has been seriously explored (Bernstein and Kaxiras 1996; Yang, Mehl, and Papaconstantoupolos 1998).

Recently (Krasko, to be published), it was suggested that the virial theorem, as applied to a condensed-matter system, enabled one to directly interpret the ingredient contributions to the embedded-atom method (EAM): the pair potential and the embedded function, in terms of the density-functional theory. This interpretation also suggests a way of developing a fundamentally new method for atomistic simulations that can be called “semi-*ab-initio*.” This method would be using the virial-theorem density-functional expression for the total energy, the electron charge density being the only “adjustable” quantity. The method would be applicable both to pure crystals, compounds, and systems with impurities. Angular-dependent interatomic interaction would also be automatically included in a natural way. The present technical report summarizes the first attempts at developing such a method.

The work summarized in this technical report has been done during the author’s stay with the Department of Nuclear Engineering, MIT, Cambridge, MA, as a visiting scholar, in academic year 1997–1998.

## 2. Theoretical Background of the New Method

As mentioned above, in its traditional implementation, the density-functional approach requires solving a self-consistent Kohn-Sham quasi one-particle Schrödinger equation. As for the exact density functional, or the spin-density functional (SDF) for the total energy,  $E\{\rho(\mathbf{r})\}$  [where  $\rho(\mathbf{r})$  is the electron density at point  $\mathbf{r}$ ], its explicit form is not known and may never be.

In the recent years, the interest toward finding a meaningful approximation for the SDF, using various versions of “orbital free” kinetic energy (KE) functionals has been awakened (e.g., Wang and Teter 1992; Pearson, Smargiassi, and Madden 1993; Smargiassi and Madden 1994).

On the other hand, the SDF, in what can be called a “reduced” form, can easily be found using the scaling procedure usually involved in formulating the virial theorem (Ross 1969). In this section, we show how such a reduced SDF can be found.

The total energy functional,  $E\{\rho(\mathbf{r})\}$ , is, as usual,

$$E\{\rho(\mathbf{r})\} = T\{\rho(\mathbf{r})\} + U\{\rho(\mathbf{r})\} + E_{xc}\{\rho(\mathbf{r})\}, \quad (1)$$

where  $T\{\rho(\mathbf{r})\}$ ,  $U\{\rho(\mathbf{r})\}$ , and  $E_{xc}\{\rho(\mathbf{r})\}$  are, respectively, the KE of noninteracting electrons and the potential and exchange-correlation energy functionals. Note that here,  $\rho(\mathbf{r})$  may be a trial density.

The potential energy functional is

$$U = \int V(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + 1/2 \int \int \rho(\mathbf{r}) \rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'| d\mathbf{r} d\mathbf{r}' + E_{es}, \quad (2)$$

where  $V(\mathbf{r})$  is the “external” (electron-ion) potential, and  $E_{es}$  is the electrostatic ion-ion interaction energy. As for  $E_{xc}\{\rho(\mathbf{r})\}$ , we suppose that it is known either in a local density approximation (LDA) (Hohenberg and Kohn 1964) or the so-called “generalized gradient approximation” (GGA) (Perdew, Burke, and Ernzerhof 1996):

$$E_{xc} = \int \rho(\mathbf{r}) \epsilon_{xc}(\mathbf{r}) d\mathbf{r}, \quad (3)$$

where  $\epsilon_{xc}(\mathbf{r}) = \epsilon_{xc}(\rho(\mathbf{r}))$  in LDA and  $\epsilon_{xc}(\rho(\mathbf{r}), t, s)$  in GGA (where  $t$  and  $s$  are the dimensionless density gradient variables).

Following the scaling procedure used by Ross (1969), let us introduce the dimensionless coordinates  $\tau = \mathbf{r}/\Omega^{1/3}$ .

Then,

$$\rho(\mathbf{r}) \rightarrow \rho(\tau)/\Omega ,$$

$$U(\rho(\mathbf{r})) \rightarrow U\{\rho(\tau)\}/\Omega^{1/3} , \text{ and}$$

$$E_{xc}\{\rho(\mathbf{r})\} \rightarrow \Omega \int (\rho(\tau)/\Omega) \epsilon_{xc}(\tau) d\tau \quad (4)$$

(the GGA dimensionless gradient variables  $t$  and  $s$  are independent of volume). The KE of noninteracting electrons is

$$T(\tau) = \sum_{occ} \int \phi_i(\tau)^* (1/2) \nabla^2 \phi_i(\tau) d\tau , \quad (5)$$

where  $\phi_i(\tau)$ 's are the (trial) one-electron wave functions and the summation is extended to all occupied states. Hence,  $T$  scales as

$$T\{\rho(\mathbf{r})\} \rightarrow T(\tau)/\Omega^{2/3} . \quad (6)$$

Now, let us calculate  $P = -dE\{\rho(\mathbf{r})\}/d\Omega$ :

$$P = 2/3 T/\Omega - d(U + E_{xc})/d\Omega . \quad (7)$$

The volume derivative is easily taken using the scaling equations (4) and (6):

$$\begin{aligned} d(U + E_{xc})/d\Omega &= -U(\Omega)/(3\Omega) \\ &+ 1/\Omega \int [\rho(\mathbf{r}) \epsilon_{xc}(\mathbf{r}) - \rho^+(\mathbf{r}) \mu_{xc}^+(\mathbf{r}) - \rho^-(\mathbf{r}) \mu_{xc}^-(\mathbf{r})] d\mathbf{r} \end{aligned} \quad (8)$$

If  $\rho(\mathbf{r})$  is the exact solution of the Kohn-Sham equation (the minimizer of the SDF), then  $\mathbf{P} = \mathbf{P}$ , the physical pressure, and equation (7) is just one of the versions of the virial theorem. It may be represented in the traditional form (Slater 1972; Janak 1974) using equation (8):

$$2T = 3 \mathbf{P}\Omega - U + 3 \int [\rho(\mathbf{r}) \epsilon_{xc}(\mathbf{r}) - \rho^+(\mathbf{r}) \mu_{xc}^+(\mathbf{r}) - \rho^-(\mathbf{r}) \mu_{xc}^-(\mathbf{r})] d\mathbf{r}. \quad (9)$$

In equation (8) and here,

$$\mu_{xc}^{+-}(\mathbf{r}) = \delta E_{xc} / \delta \rho^{+-}(\mathbf{r}) \quad (10)$$

is the exchange-correlation one-electron potential ( $^{+-}$  stands for spin polarization). The expression for the exchange-correlation part of equation (9), here, is more general than that for non-spin-polarized systems in Janak (1974). Since the GGA gradient variables do not depend on volume, equation (9) is also the expression for the virial theorem in GGA.

We again stress that both the scaling, equations (4) and (6), and the taking of the derivative over the volume are valid not for just the SDF of stationary electron density,  $\rho(\mathbf{r})$  but for any appropriate trial density. In what follows,  $\rho(\mathbf{r})$  means just such, a trial density.

It should be also stressed that, although the virial theorem, equation (9), is also valid for trial densities (then  $\mathbf{P}$  has to be substituted for  $P$ ), it is satisfied for a real physical pressure  $P$  only if  $\rho(\mathbf{r})$  is a highly accurate solution of the corresponding Kohn-Sham equation.

Let us return to equation (7). We have

$$T = 3/2 \mathbf{P}\Omega + 3/2 \Omega d(U + E_{xc})/d\Omega. \quad (11)$$

If  $\mathbf{P} = 0$ , then

$$T = 3/2 \Omega_0 d(U + E_{xc})/d\Omega|_{\Omega=\Omega_0} , \quad (12)$$

where  $\Omega_0$  is the volume corresponding to  $P = 0$ .

For an arbitrary volume,  $\Omega$ , the noninteracting electron KE, due to the scaling, equation (6), equals

$$T(\Omega) = [3/2 \Omega_0 d(U + E_{xc})/d\Omega|_{\Omega=\Omega_0}] (\Omega_0/\Omega)^{2/3} \quad (13a)$$

or, making use of equation (8),

$$T(\Omega) = (\Omega_0/\Omega)^{2/3} \{ -1/2 U(\Omega_0) + 3/2 \int [\rho(\mathbf{r}) \epsilon_{xc}(\mathbf{r}) - \rho^+(\mathbf{r}) \mu_{xc}^+(\mathbf{r}) - \rho^-(\mathbf{r}) \mu_{xc}^-(\mathbf{r})] d\mathbf{r}|_{\Omega=\Omega_0} \} . \quad (13b)$$

Finally, the total energy functional is

$$E(\Omega) = U + E_{xc} + 3/2 \Omega (\Omega_0/\Omega)^{5/3} d(U + E_{xc})/d\Omega|_{\Omega=\Omega_0} \quad (14a)$$

or, in the explicit form,

$$E(\Omega) = U + E_{xc} + (\Omega_0/\Omega)^{2/3} \{ -1/2 U(\Omega_0) + \Delta_{xc}|_{\Omega=\Omega_0} \} , \quad (14b)$$

where

$$\Delta_{xc} = 3/2 \int [\rho(\mathbf{r}) \epsilon_{xc}(\mathbf{r}) - \rho^+(\mathbf{r}) \mu_{xc}^+(\mathbf{r}) - \rho^-(\mathbf{r}) \mu_{xc}^-(\mathbf{r})] d\mathbf{r} . \quad (15)$$

Then, the “pressure” equals

$$P(\Omega) = -d(U + E_{xc})/d\Omega + (\Omega_0/\Omega)^{5/3} d(U + E_{xc})/d\Omega|_{\Omega=\Omega_0} \quad (16a)$$

or

$$P(\Omega) = 1/(3\Omega) \{-U(\Omega) + 2 \Delta_{xc} - (\Omega_0/\Omega)^{2/3} [-U(\Omega_0) + 2 \Delta_{xc}|_{\Omega=\Omega_0}]\}. \quad (16b)$$

Equations (14a) and (14b) are the reduced SDF that we sought. It is an explicit functional of  $\rho(\mathbf{r})$  valid for any appropriate trial density. For a stationary density (satisfying a Kohn-Sham equation), equations (7) and (9) are equivalent to the virial theorem and equations (14a) and (14b) just “recalculate” the total energy, which has to be equal to that following from the traditional Kohn-Sham method. Equation (16) is then the equation of state.

Of course, the reduced SDF does not contain all the information of the general universal SDF. However, it may serve as a basis for a fundamentally new approach toward developing semi-*ab-initio* methods of atomistic simulations.

In the next section, we outline the algorithm of constructing the model density and the procedure of calculating the total energy, which lies at the core of the new proposed method.

### 3. Formulation of the Method

Suppose that the ground-state electron density may be written as a superposition of “atomic” (or “pseudo-” or “quasi-atomic”) densities:\*

$$\rho(\mathbf{r}) = \sum_{\mathbf{R}} \rho^0(|\mathbf{r} - \mathbf{R}|). \quad (17)$$

This ansatz has, in the past, been studied in great detail. It was, in particular, shown (Chetty, Jacobsen, and Nørskov 1991) that optimized and transferable atomic densities can be found from

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\* There is no unique and exact way of subdividing the total electron charge density into a superposition of atomic densities. In fact, by introducing Wannier functions, one can show that, in general, the electron charge density cannot be represented exactly as the superposition of neighbor-centered positive functions that could be interpreted as individual atomic densities; it is possible only for insulators (Krasko, to be published).

the first principles. Equation (17) is the main approximation of our method. A procedure of constructing  $\rho^0(|\mathbf{r} - \mathbf{R}|)$  is discussed next. The ansatz, equation (17), also enables one (Krasko 1999) to interpret the potential energy contributions to  $E^0$ , equation (10), in an intuitively appealing form, the one similar to that of the EAM.

Using equation (17), the potential energy,  $U$ , equation (2), can be written down in terms of an effective pair potential:

$$1/2U = E^0 + 1/2 \sum_{\mathbf{R} \neq \mathbf{R}'} V(\mathbf{R} - \mathbf{R}') . \quad (18)$$

The first term depends only on the volume but not the atomic coordinates (we give its explicit expression later). The second term is the pair interaction energy with the pair potential:

$$\begin{aligned} V(\mathbf{R}) = & -1/(2\pi^2) \int d\mathbf{q} Z \rho^0(\mathbf{q})/q^2 \exp(i\mathbf{q} \cdot \mathbf{R}) \\ & + 1/(4\pi^2) \int d\mathbf{q} |\rho^0(\mathbf{q})|^2/q^2 \exp(i\mathbf{q} \cdot \mathbf{R}) + Z^2/|\mathbf{R}| . \end{aligned} \quad (19)$$

Here and below,  $\rho^0(\mathbf{q})$  is the Fourier transform of the atomic charge density,  $\rho^0(\mathbf{r})$  and the integration extends over all the reciprocal space.

The exchange-correlation contribution,  $\Delta_{xc}$ , to the total energy,  $E_{xc}$ , from equation (3),

$$\Delta_{xc} = 3/2 \int \rho(\mathbf{r}) [\varepsilon(\mathbf{r}) - \mu(\mathbf{r})] d\mathbf{r}, \quad (20)$$

cannot, however, be represented in terms of an interatomic potential.

Finally the total energy, equation (14b), can be rewritten as

$$\begin{aligned} E = & E^0 + 1/2 (1 - 1/2 (\Omega_0/\Omega)^{1/3}) \sum_{\mathbf{R} \neq \mathbf{R}'} V(\mathbf{R} - \mathbf{R}') \\ & + E_{xc} + (\Omega_0/\Omega)^{2/3} \Delta_{xc} \{\rho(\mathbf{r})\}_{\Omega=\Omega_0} . \end{aligned} \quad (21)$$

Here,

$$E^0 = -N (1 - 1/2 (\Omega_0/\Omega)^{1/3}) \{1/(4\pi^2) \int d\mathbf{q} \rho^0(\mathbf{q})/q^2 + 1/(8\pi^2) \int d\mathbf{q} |\rho^0(\mathbf{q})|^2/q^2\} \quad (22)$$

(N is the total number of atoms in the simulation volume). The origin of this energy contribution is obvious; it is the atomic "self-interaction," the term corresponding to  $\mathbf{R} = \mathbf{R}'$ , which has been excluded from the pair potential sum in equation (20).

Now, we proceed with formulation of the suggested method. As was mentioned previously, our goal is to parametrize the atomic density,  $\rho^0(\mathbf{r})$ .

Since it is desirable to represent the density as exactly as possible, it is appealing to separate the contributions of the core and the valence electrons:

$$\rho^0(|\mathbf{r}|) = \rho_{\text{cor}}^0(|\mathbf{r}|) + \rho_{\text{val}}^0(|\mathbf{r}|) . \quad (23)$$

$\rho_{\text{cor}}^0(|\mathbf{r}|)$  will be approximated once and for all for the given atom using the results of *ab-initio* calculations. Let

$$\rho_{\text{cor}}^0(|\mathbf{r}|) = A_{\text{cor}} \sum_i \{c_i^0 + c_i^1 r + c_i^2 r^2 + \dots\} \exp(-\lambda_i^c r) . \quad (24)$$

Here,  $A_{\text{cor}}$  is the normalization constant (securing the right number of core electrons), and  $c_i^j$ 's and  $\lambda_i^c$ 's are the parameters to be found by root-mean-square (rms)-fitting of equation (24) to the calculated core densities (depending on the core structure, there may be a few different "subshells,"  $i$ ).

The valence charge density will be approximated by the same class of functions:

$$\rho_{\text{val}}^0(|\mathbf{r}|) = A_{\text{val}} \sum_i \{v_i^0 + v_i^1 r + v_i^2 r^2 + \dots\} \exp(-\gamma_i^v r) , \quad (25)$$



where  $A_{\text{val}}$ , again, is the normalization constant (securing the right number of valence electrons) and  $v_i^j$ 's and  $\gamma_i^y$ 's are the adjustable parameters. In a transition metal, one may expect three different subshells,  $i$ , corresponding to  $-s$ ,  $-p$ , and  $-d$  electrons.

The chosen class of functions is convenient, since it allows the integration to be performed analytically when calculating both the Fourier transforms of the densities and the effective pair potential, equation (19), and the structure-independent term,  $E^0$ , equation (22). (We are not writing down those lengthy formulae here).

Thus, the first two contributions to  $E$ , equation (21), can easily be found in analytic form. The calculation of the third and fourth terms to do with exchange correlation is less straightforward. First of all, an exchange-correlation model (either local or GGA) has to be chosen among a few models being currently used in *ab-initio* methods. The corresponding subroutine [having  $\rho(\mathbf{r})$  as an input and  $\epsilon(\mathbf{r})$  and  $\mu(\mathbf{r})$  as outputs] may be borrowed from any *ab-initio* code in the public domain. What is important is that the same exchange-correlation approximation be used both in evaluating  $\Delta_{\text{xc}}$  and all the *ab-initio* calculations used in the method calibration. We suggest to use the most advanced exchange-correlation model, GGA (Perdew, Burke, and Ernzerhof 1996).

The calculation of the exchange-correlation contribution in equation (21), should be performed as follows. Within the "simulation volume," a grid of coordinates  $\{\mathbf{r}\}$  is to be constructed. Based on our experience with *ab-initio* calculations, a nonuniform grid has to be used, with the grid points thickening around the lattice sites,  $\{\mathbf{R}\}$ , and being looser in the interstitial volume.\* Then, the total density,  $\rho(\mathbf{r})$ , as a superposition of  $\rho^0(|\mathbf{r} - \mathbf{R}|)$ 's is calculated on this grid. Computationally, this is to be a rather fast procedure since, typically,  $\rho^0(|\mathbf{r} - \mathbf{R}|)$  virtually completely decays by the third shell of neighbors. As the last step in the calculation of the exchange-correlation contributions to the total energy, the integrations are to be performed using one of the available methods of numerical three-dimensional (3-D) integration.

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\* Recently, a more sophisticated way of introducing an "adaptive" coordinate system was suggested; see Modine, Zumbach, and Kaxiras (1997).

The main idea behind the reduced SDF is to scale the KE functional and thus make use of the virial theorem. As a result, the knowledge of the electron charge density (as well as both the potential and the exchange correlation contributions) at  $P = 0$ , or  $\mathbf{P} = 0$  becomes a necessity. Therefore, in every calculation of the total energy at a given atomic configuration and simulation volume, a part of the calculation must be performed at an “equilibrium” volume,  $\Omega_0$ . This volume, however, is unknown.

We suggest the following procedure of finding  $\Omega_0$ . The total energy at volume  $\Omega$ , equation (21), depends on  $\Omega_0$ . We may consider  $\Omega_0$  as a variational parameter and minimize equation (21) at fixed  $\Omega$ , with respect to  $\Omega_0$ . The obtained value will also automatically satisfy equation (16b) at  $P = 0$ .

In order to deal with both an arbitrary volume and  $\Omega_0$ , we again, use a scaling procedure. Let  $\Omega_r$  be a “reference” simulation volume. Actually,  $\Omega_r$  can be any volume within the range of physically meaningful volumes. Then the arbitrary volume can be represented as

$$\Omega = \varpi^3 \Omega_r \quad (26)$$

where  $\varpi$  is a scaling factor. Then, all the distances in our model will be scaled uniformly, and the density, equation (17), corresponding to the volume,  $\Omega$ , is found simply by multiplying all the  $\mathbf{r}$ 's and  $\mathbf{R}$ 's by  $\varpi$ . Suppose  $\Omega$  is the volume at which the total energy, equation (21), is to be calculated. The equilibrium volume,  $\Omega_0$ , is then the volume corresponding to the minimum of the total energy, equation (21), at fixed  $\Omega$ . Obviously, it would correspond to the scaling factor  $\varpi_0$ :

$$\Omega_0 = \varpi_0^3 \Omega. \quad (27)$$

Thus, we have found the equilibrium volume,  $\Omega_0$ . From this point on, the procedure of calculating the total energy, equation (21), is straightforward.

This completes the procedure of calculating the total energy of the system.

We now summarize the method outlined previously. Suppose we want to calibrate the method for transition metal Mo. The following steps will have to be followed.

- (1) We begin by performing a series of *ab-initio* calculations for body-centered cubic (bcc) (e.g., FLAPW [Singh 1994]) to find  $E^{\text{bcc}}(\Omega)$  and  $\Omega_0^{\text{bcc}}$  ( $P = 0$ ). Repeat the previous calculations for face-centered cubic (fcc), hexagonal close-packed (hcp), and, possibly, a low-symmetry hypothetical phase (HP) of Mo, and find  $E^{\text{fcc}}(\Omega)$ ,  $E^{\text{hcp}}(\Omega)$ ,  $E^{\text{HP}}(\Omega)$  and the  $P = 0$  volumes:  $\Omega_0^{\text{fcc}}$ ,  $\Omega_0^{\text{hcp}}$ ,  $\Omega_0^{\text{HP}}$ . These calculations also generate the core charge densities to be used in the next step.
- (2) Approximate the Mo core electron density using equation (24) and find the appropriate parameters by rms-fitting the function to the calculated *ab-initio* Mo core density.
- (3) After the previous *ab-initio* calculations have been performed, we have six equations for fitting the parameters of the valence electron density, equation (24): three for the  $P = 0$  energies of the three phases [we need to calculate only  $E$ , equation (21)] and three equations  $P(\Omega_0) = 0$ . Some more equations may be used; for example, fitting the total energy to the *ab-initio* energies for other HPs or the elastic moduli:  $C_{11}$ ,  $C_{12}$ ,  $C_{44}$ , and  $B$  (we do not write out the corresponding formulae, as well as the expression for the force on each atom; they are quite straightforward but require a tedious algebra).
- (4) Having solved this system of simultaneous equations, one will find the coefficients in the approximation, equation (25). The more complicated procedure of finding  $\Omega_0$  will be necessary for atomistic simulations outside the *ab-initio* calibration.
- (5) Now, with all the coefficients in equations (24) and (25) known, the calibration of the method is completed and one may proceed with atomistic simulations of the system of interest.

As an example of such a system, let us consider a grain boundary. Let the simulation volume (for the unrelaxed GB) be  $\Omega$  that contains  $N$  atoms. The Mo atoms take positions  $\{\mathbf{R}\}$ . First, we calculate  $\Omega_0$  by minimizing  $E$ , equation (21), at the fixed simulation volume  $\Omega$ , with respect to  $\Omega_0$ .

In order to analyze the atomic relaxation, one has to calculate the forces on each atom, then vary the atomic positions  $\{\mathbf{R}\}$  toward the state of mechanical equilibrium (forces equal zero), and repeat calculations until an absolute energy minimum has been achieved. On each step of shifting the atomic positions, the new  $\Omega_0$  has to be calculated using the previously outlined procedure.

Here, we should again stress that the total energy, equation (21), does have the variational properties with respect to the electron charge density. Therefore, the minimization to be performed does mean finding the density that would correspond to the energy minimum, albeit in a restricted manifold of the superpositions of "atomic densities," equation (17). Thus, the precision of the method as a whole depends chiefly on the generation of realistic density, equation (17).

In the next section, we show how the method, in a natural way, can be generalized to a two-component system: a crystal with impurity atoms or a compound.

## **4. Generalization of the Method to Two-Component Systems**

The general formalism of the virial theorem is valid, irrespective of the system it is applied to. The difference between a one-component and a two-component (or, for that matter, a multicomponent) system is only in how the electron density,  $\rho(\mathbf{r})$ , is represented.

Let the system be a substitutional solid solution of components A and B (the generalization to interstitial solid solution is straightforward). Then, the electron charge density at a given point can be written as a generalized ansatz:

$$\rho(\mathbf{r}) = \sum_{\mathbf{R}} \{C_A(\mathbf{R})\rho_A^0(\mathbf{r} - \mathbf{R}) + C_B(\mathbf{R})\rho_B^0(\mathbf{r} - \mathbf{R})\}. \quad (28)$$

The "external," ion-electron potential is

$$V(\mathbf{r}) = \sum_{\mathbf{R}} \{C_A(\mathbf{R}) Z_A + C_B(\mathbf{R}) Z_B\} / |\mathbf{r} - \mathbf{R}|, \quad (29)$$

where  $C_A(\mathbf{R})$  and  $C_B(\mathbf{R})$  are the random quantities taking the value 1 if, respectively, an atom A or an atom B sits in the site  $\mathbf{R}$ ; and 0 otherwise ( $C_A(\mathbf{R}) + C_B(\mathbf{R}) = 1$ ),  $\rho_A^0(\mathbf{r} - \mathbf{R})$ , and  $\rho_B^0(\mathbf{r} - \mathbf{R})$  are, as before, the atomic densities and  $Z_A$  and  $Z_B$  are the nuclei charges of atoms A and B.

Then  $E$  [a counterpart of equation (21)] can be written in terms of effective pair potentials as

$$\begin{aligned} E = E^0 &+ 1/2 (1 - 1/2 (\Omega_0/\Omega)^{1/3}) \sum_{\mathbf{R} \neq \mathbf{R}'} \{C_A(\mathbf{R})C_A(\mathbf{R}')V_{AA}(\mathbf{R} - \mathbf{R}') \\ &+ C_B(\mathbf{R})C_B(\mathbf{R}')V_{BB}(\mathbf{R} - \mathbf{R}') + 2 C_A(\mathbf{R})C_B(\mathbf{R}')V_{AB}(\mathbf{R} - \mathbf{R}')\} \\ &+ E_{xc} + (\Omega_0/\Omega)^{2/3} \Delta_{xc}\{\rho(\mathbf{r})\}|_{\Omega=\Omega_0}, \end{aligned} \quad (30)$$

where  $E_{xc}$  and  $\Delta_{xc}\{\rho(\mathbf{r})\}$  are defined by the same expressions, equations (3) and (15) but with the density  $\rho(\mathbf{r})$  obeying the new ansatz, equation (28).

The first term, again, depends only on volume:

$$E^0 = -1/(4\pi^2) \langle Z \rangle \int d\mathbf{q} \langle \rho^0(\mathbf{q}) \rangle / q^2 + 1/(8\pi^2) \int d\mathbf{q} \langle |\rho^0(\mathbf{q})|^2 \rangle / q^2, \quad (31)$$

where

$$\langle Z \rangle = c_A Z_A + c_B Z_B,$$

$$\langle \rho^o(\mathbf{q}) \rangle = c_A \rho_A^o(\mathbf{q}) + c_B \rho_B^o(\mathbf{q}) ,$$

and

$$\langle |\rho^o(\mathbf{q})|^2 \rangle = c_A |\rho_A^o(\mathbf{q})|^2 + c_B |\rho_B^o(\mathbf{q})|^2 . \quad (32)$$

Also,  $c_A$  and  $c_B$  are the atomic fractions of atoms A and B:

$$c_A = \sum_{\mathbf{R}} C_A(\mathbf{R}) / N$$

and

$$c_B = \sum_{\mathbf{R}} C_B(\mathbf{R}) / N ,$$

where  $N$ , again, is the total number of atoms in the simulation volume. The effective interatomic potentials then are defined as ( $\alpha, \beta = A, B$ ):

$$\begin{aligned} V_{\alpha\beta}^c(\mathbf{R}) = & -Z_{\alpha}/(2\pi^2) \int d\mathbf{q} \rho_{\beta}^o(\mathbf{q})/q^2 \exp(i\mathbf{q}\cdot\mathbf{R}) \\ & + 1/(4\pi^2) \int d\mathbf{q} \rho_{\alpha}^o(\mathbf{q}) \rho_{\beta}^o(\mathbf{q})^*/q^2 \exp(i\mathbf{q}\cdot\mathbf{R}) + Z_{\alpha} Z_{\beta}/|\mathbf{R}| . \end{aligned} \quad (33)$$

The formulation of the method for two-component systems is virtually the same as that outlined before. Now one has two core densities:  $\rho_{\text{cor}}^{o,A,B}$ , and two valence densities:  $\rho_{\text{val}}^{o,A,B}$ . The calibration and implementation of the method is similar to those in one-component case; the only difference being that the number of fitting equations doubles and the equations have to reflect some representative high- and low-symmetry two-component configurations.

## 5. Conclusion

To summarize, we suggest a semi-*ab-initio* method for atomistic simulations based on the virial theorem. The method is completely within the realm of the density-functional theory. The

crucial component of the method is ansatz equation (17) [or equation (28) for a two-component system] expressing the electron density at point  $\mathbf{r}$  as a superposition of atomic densities due to the neighboring atoms. If, upon calibrating the method, the  $E$ 's are fitted to the equilibrium energies of a few crystal modifications, the electron densities found by the atomic densities superposition for those modification are very close to the "true" stationary densities that could be found from an *ab-initio* calculation. Thus, the success of the method will depend on whether the charge density in a low-symmetry system under simulation is also close to the true density that could be obtained from a meaningful *ab-initio* calculation; then, the results of the simulation would be identical to those of the corresponding *ab-initio* calculation. To what extent the superposition ansatz satisfies this condition is unclear, *a priori* testing and experimentation are necessary. As was mentioned previously, according to Chetty, Jacobsen, and Nørskov (1991), meaningful transferable *ab-initio* atomic densities could be found.

Regarding the separation of core and valence densities [equations (23)–(25)], a note should be added. "Fixing" the core density is reminiscent of a so-called "frozen core" approximation. When the frozen-core approximation is involved in an *ab-initio* method, the virial theorem is not valid. The reason for this failure is that, while the frozen core potential is treated as a part of the external potential, the exchange-correlation core-valence interaction is also preserved (the virial theorem would be valid again if the latter were dropped). In our case, however, the frozen core is a part of the total electron density and it is the *total* electron density that is subject to "fitting" to the *ab-initio* density. In fact, from the physical point of view, it would probably be more logical if the calibration of the method consisted in directly fitting the model density to the *ab-initio* density rather than requiring that the calculated and *ab-initio* energies were equal. We are going to explore this path also in a subsequent paper.

As was already mentioned, the new method is quite versatile. If additional *ab-initio* information about the system of interest is available, it can be easily implemented to make the method more realistic. As an example, while doing simulations on diamond-type semiconducting crystals, it would be helpful (perhaps even necessary) to introduce, as a separate electron density, the so-called "bond charges" (Phillips 1973). The method can also be applied to atomistic simulation of ferromagnetic systems; in that case, the separate spin-up and spin-down

densities have to be introduced (the exchange-correlation contributions to the energy can be easily generalized for a spin-polarized case).

An important feature of the method is that it automatically allows for "directional bonds." In spite of the fact that, in the suggested implementation, the total valence charge is a superposition of spherically symmetric charges,  $\rho(\mathbf{r})$  does have the symmetry of the crystal lattice, thus incorporating all "directionality" features. It is interesting, however, that the effective pair potential, equation (19) (and its counterparts for two-component system), is lacking directionality. Since the Fourier transform of the density,  $\rho(\mathbf{q}) = \rho(|\mathbf{q}|)$ , the angle integrations in equation (19) are straightforward, resulting in the remaining integral in equation (19) having the integrand that is proportional to  $\sin(qR)/(qR)$ , where  $q$  and  $R$  are the moduli of the corresponding vectors. As a result, the pair potential depends only on the distance:

$$V(\mathbf{R}) = V(|\mathbf{R}|) .$$

In fact, that is what is to be expected of a pair potential; if the space is isotropic, the two atoms interacting via a pair potential do not have to know anything about their environment since no special direction has been singled out.

The directionality, however, is completely preserved in the exchange-correlation contribution,  $\Delta_{xc}\{\rho(\mathbf{r})\}$ , equation (15), through the symmetry of  $\rho(\mathbf{r})$ .

As was previously mentioned, the method is quite versatile, and, if necessary, nonspherically symmetric atomic densities may be introduced (Löwdin 1956).



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